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# Investigation of the effects of fatty acids on the compressive strength of the concrete and the grindability of the cement

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**Abstract**

In cement industry, a great energy consumption has been observed during grinding of clinker. To reduce this consumption, some waste products have been used as grinding aids.

In this investigation, the effects of sunflower oil (SO), oleic acid (OA), stearic acid (SA), myristic acid (MA) and lauric acid (LA) on the fineness and strength of the cement have been examined. These aids were added into clinker in certain ratios based on the cement clinker weight and the grinding has been done for a definite time at the same condition.

All of the fatty acids used increased the fineness as compared with the cement without the grinding additives. SO and OA decreased the strength significantly, LA decreased it to a lesser extent and SA increased it definitely according to the common cement. But MA did not alter the strength of the cement as much as SA. In addition, the covering of the balls influences the grinding of cement clinker unfavourably.


*Keywords:* Grinding; Cement clinker; Compressive strength; Surface area; Fatty acids

## 1. Introduction

In the cement industry, a great amount of the total electric energy consumption is consumed in grinding the raw materials and the clinker. Because of the diminishing available sources of energy and the attendant rise in energy costs, it is important to pay particular attention to this major cost item. In the cement industry, in order to reduce the energy cost, grinding aids are used. The most important functions of the chemical aids are to eliminate or retard the caking and agglomeration phenomena during the grinding process. In the cement industry, there are so many different materials used as grinding aids, including solids, such as graphite, oleoresinous liquid materials, volatile solids, and vapors [1–3]. From the chemical engineer's point of the view, there are very interesting studies in the literature. Among those studies, Serafin [4] and Fagerholt [6] reported that triethanolamine and phenol increased the Blaine surface area of the cement and the mill output. Lange [5] revealed that the use of diethylene glycol facilitated the grinding of portland masonry cement. Schenker et al. [7] found that addition of 0.4 wt.% of a first-run distillation product from trimethylolpropane manufacture to a standard cement mix before grinding improved the Blaine surface. Nikl and Marek [8] announced that size reduction of cement in the presence of the aqueous solution of phenolsulfonic acid or ethylbenzenedisulfonic acid gave products with specific surface increased by approximate 10%. Surana and Joshi [9] explained that the specific surface of a sample containing cement clinker, china clay and gypsum ground with 0.05% urea in the aqueous solution is 755 $cm^2/g$ higher than that of a sample without the grinding aid. The effect of methyl alcohol, ethyl alcohol, acetone, benzene, diethyl ether on the grinding of cement clinker in a ball mill was investigated by Kim [10] and it was found that methyl and ethyl alcohol provided practical power saving and all of the aids decreased the compressive strength. Shakhbazyan and Mikhaelyan [11] analyzed the effect of the wastes composed

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of activated carbon and zinc acetate on the specific surface area of the ground clinkers. Furthermore, 0.08–0.5% hydrophobic agents based on the weight of clinker, such as calcium oleate, naphthenate, laurate, stearate or palmitate, or the free acids themselves are used at the clinker–gypsum grinding stage. But they may cause some retardation of setting [12]. Moreover, Hekal et al. [13,14] examined the mechanical and physicochemical properties of hardened portland cement pastes containing hydrophobic admixtures. In addition, the waterproofing characteristics of polymer-modified portland cement mortars have been studied by Saija [15]. Besides these references, as known, whether the additives used reduce the compressive strength according to the normal cement or not is very important.

The main aim in this research is to investigate the effects of sunflower oil (SO) acid, oleic acid (OA), stearic acid (SA), myristic acid (MA) and lauric acid (LA) on the specific surface and the compressive strength of the normal cement.

## 2. Experimental

### 2.1. Materials

Sunflower oil, oleic acid, lauric acid, myristic acid and stearic acid were supplied from Alemdar Chemical Industry, Gebze, Turkey. All the grinding additives used in this study are very cheap renewable chemicals, and obtained mostly from natural sources. For example, stearic acid, hard, white, waxlike solid of the composition $CH_3(CH_2)_{16}COOH$ melting at 69 °C, obtained from vegetable fats and oils. Myristic acid is a hard crystalline solid of the composition $CH_3(CH_2)_{12}COOH$ melting at 58 °C, obtained from coconut oil. Lauric acid occurs in high percentage in the oil of the coconut and other kernels of the tropical palm nuts. It is a saturated acid of the composition $CH_3(CH_2)_{10}COOH$ and is a semisolid melting at 44 °C. Oleic acid occurs in most natural fats and oils in the form of the glyceride. It is a complex acid and the composition of $CH_3(CH_2)_7CH$: $CH(CH_2)_7COOH$. Sunflower oil contains about 66% linoleic acid, 23% oleic acid, 4 % stearic acid and 6% palmitic acid. The chemical composition of the cement clinker and the properties of the balls are also given in Table 1.

Table 1
Chemical analysis and properties of materials

| Cement clinker | | The size distribution of the balls | | |
|---|---|---|---|---|
| Components | wt.% | Diameter (mm) | Total ball weight (kg) | Total ball number |
| $SiO_2$ | 22.18 | 60 | 4.343 | 5 |
| $Al_2O_3$ | 5.57 | 50 | 2.541 | 5 |
| $Fe_2O_3$ | 3.56 | 40 | 1.540 | 6 |
| CaO | 65.76 | 30 | 1.689 | 16 |
| MgO | 1.22 | 20 | 4.329 | 154 |
| $SO_3$ | 0.45 | 10 | 8.830 | 771 |
| $Cl^-$ | 0.0140 | | | |
| Loss on ignition | 0.31 | | | |
| $Na_2O$ | 0.22 | | | |
| $K_2O$ | 1.03 | | | |
| $TiO_2$ | 0.28 | | | |
| Free CaO | 1.2 | | | |
| Hydraulic module | 2.1 | | | |
| Silicate module | 2.429 | | | |
| Alumina module | 1.563 | | | |
| Lime standard | 92.185 | | | |
| $C_3S$ | 49.51 | | | |
| $C_2S$ | 25.13 | | | |
| $C_3A$ | 8.58 | | | |
| $C_4AF$ | 10.65 | | | |

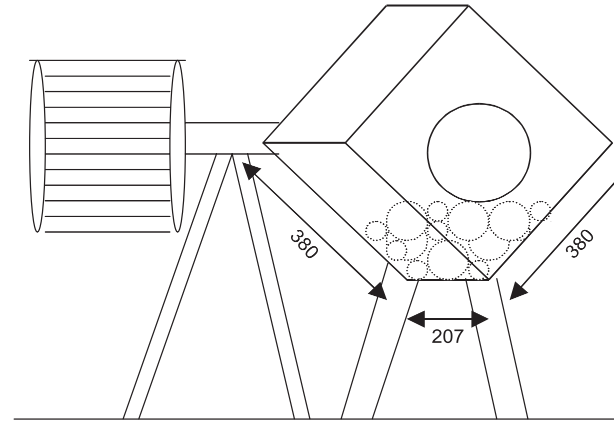

Fig. 1. The view of the box mill.

### 2.2. Methods

The total weight of 2000 g of the mixture was used for each experimental run. The mixture of 95% clinker (1900 g) and 5% limestone (100 g) was first put in the box mill. The total space volume of the box mill was 29.9 l. The balls occupied 17% of the space volume of the box mill. The speed and the grinding run time were 47 rpm, and 45 min, respectively. The shape and the dimensions of the box mill are given in Fig. 1.

#### 2.2.1. Determination of fineness

The fineness was determined as the percent retained by sieving a sample of 10 g cement ground on 0.045, 0.090 and 0.200 mm screen opening according to ASTM C430-96 [16].

#### 2.2.2. Determination of density

First, the ground cement sample weighted (m) was filled into the sample cup and then helium gas was passed through the cup placed into a closed part of multi pycnometer (Model MVP-1). After the volume (V) of the sample was calculated, the density was found by $\rho$=m/V formula according to ASTM C 188-95 [17].

#### 2.2.3. Determination of Blaine surface

The specific surface was found by Blaine Star type ZZB/PC-MT according to ASTM C 204 [18].

*2.2.4. Determination of consistency*

Three hundred grams of the ground cement and 75 g of the tap water was mixed in a vessel with a spoon for 3 min, and then the cement paste was filled in a vicat ring on glass plate. The tip of the plunger fell onto the top surface of the cement paste and then set freely. If the used water is enough for normal consistent paste, the plunger falls to a distance of 5–7 mm from the glass plate in 30 s. By this procedure, the water quantity needed for cement was determined. The operation was performed by vicat apparatus with a cylindrical plunger according to ASTM C 187-98 [19].

*2.2.5. Determination of initial and final setting times*

This experiment was carried out by settling a needle in place of the plunger according to ASTM C 191-01a [20]. After the normal consistent cement paste was filled in the vicat ring on the glass plate, the needle of the vicat fell onto the top surface of the cement paste and the needle was tightened with a screw so as not to plunge. Upon loosening the screw, it was plunged in the different points of the cement paste every 5 min by changing the position of the vicat ring. When the needle plunging into the paste fell to a distance of 3–5 mm from the glass plate, the setting was regarded to have initiated. Accordingly, the taking time from the moment when cement and water are mixed to that when the setting is initiated was the initial setting time. After the initial setting time, the needle was plunged every 15 min and again the position of the vicat ring was changed. The final setting was determined when the needle can be plunged into 1 mm below the surface of the paste.

*2.2.6. Determination of compressive strength*

One unit of cement, including grinding aid, was mixed with three units of sand and one and a half unit of water. The mortar was placed in prismatic moulds having dimensions of 160×40×40 mm. The moulds were cured at 20 °C in a room with relative humidity of 90% for 24 h, then cured in tap water of 20 °C for 2, 7 and 28 days. After the elapsed time, the prismatic specimens were splitted and broken by a Toni Technik/Toni Norm (Model: 2020) equipment according to EN 196-1 [21,22].

## 3. Results and discussions

It is well known that the fineness of cement is a very important parameter and the increased fineness of the cement results in better strength development. However, the fineness is dependent on energy saving and economic considerations in the industry. The other important point in the grinding process, the use of the more additives than needed, can both increase the cost and affect the properties of the cement badly. Therefore, selecting an optimum amount of the addivitivies is necessary.

The water quantity, setting time, volume expansion of the cement pastes and the density of the ground mixes are shown in Table 2. The densities were measured by multi pycnometer (Model MVP-1). As a result of the increasing admixture, water percentage needed for cement paste and setting time increased, but the densities decreased. While the water percentage and final setting time for the normal cement are 26.0% and 3 h 3 min, respectively, for the cement substituted with 0.5% OA, the values were 32.5% and 4 h 10 min, respectively. However, the great variation between the values of the volume expansion was not observed. It can be concluded from this strength decrease and the physical properties that the hydration reaction of the ground cement retarded because the additives fill them by diffusing into pores and cracks in the cement particles during the grinding. Besides, it can be considered that, in water, insolubility of these aids contributes to the retardation of the hydration reaction.

Figs. 2, 3 and 4 show the variation of compressive strength versus mixture wt.% of fatty acids at 2, 7 and 28 days, respectively. The addition of both sunflower oil and oleic acid immediately decreased the compressive strength of the normal concrete approximately by 50%. The sharp decrease in compressive strength of the concrete after addition of the sunflower oil or oleic acid is very interesting. Sunflower oil contains important amounts of unsaturated oil, such as oleic acid and linoleic acid, which include double bonds. The reason for the sharp decline in the compressive strength could result from the double bonds in the structure of the fatty acids, which readily oxidizes with the dissolved oxygen of the tap water during the curing period and causes microscopic cracks in the concrete. Therefore, it is obvious that unsaturated fatty acids cannot be used as grinding agent in the manufacturing of cement.

Table 2
The physical properties of the cement mixes

| Admixture (%) | Cement (%) | Water (%) | Setting time (h:min), final | Volume expansion (mm) | Density (g/cm$^3$) |
|---|---|---|---|---|---|
| 0 | 100.0000 | 26.0 | 3:03 | 0 | 3.15 |
| 0.0125 LA | 99.9875 | 27.3 | 3:05 | – | 3.14 |
| 0.5000 LA | 99.5000 | 32.5 | 3:55 | 1 | 3.09 |
| 0.0125 MA | 99.9875 | 27.0 | 2:55 | – | 3.15 |
| 0.5000 MA | 99.5000 | 32.5 | 3:40 | 1 | 3.09 |
| 0.0250 SA | 99.9750 | 26.3 | 2:45 | 1 | 3.13 |
| 0.1000 SA | 99.9000 | 26.8 | 2:47 | 2 | 3.11 |
| 0.1500 SA | 99.8500 | 27.0 | 3:13 | 1 | 3.08 |
| 0.2000 SA | 99.8000 | 27.3 | 3:19 | 2 | 3.09 |
| 0.3000 SA | 99.7000 | 28.3 | 3:23 | 2 | 3.09 |
| 0.5000 SA | 99.5000 | 31.3 | 3:45 | 1 | 3.10 |
| 0.0250 SO | 99.9750 | 27.0 | 3:10 | 1 | 3.13 |
| 0.2000 SO | 99.8000 | 28.5 | 3:34 | 2 | 3.10 |
| 0.3000 SO | 99.7000 | 28.8 | 4:06 | 3 | 3.09 |
| 0.5000 SO | 99.5000 | 30.8 | 4:10 | 2 | 3.11 |
| 0.0250 OA | 99.9750 | 27.5 | 3:10 | – | 3.15 |
| 0.1000 OA | 99.9000 | 30.0 | 3:55 | – | 3.14 |
| 0.2000 OA | 99.8000 | 31.3 | 4:00 | – | 3.13 |
| 0.5000 OA | 99.5000 | 32.5 | 4:10 | – | 3.12 |

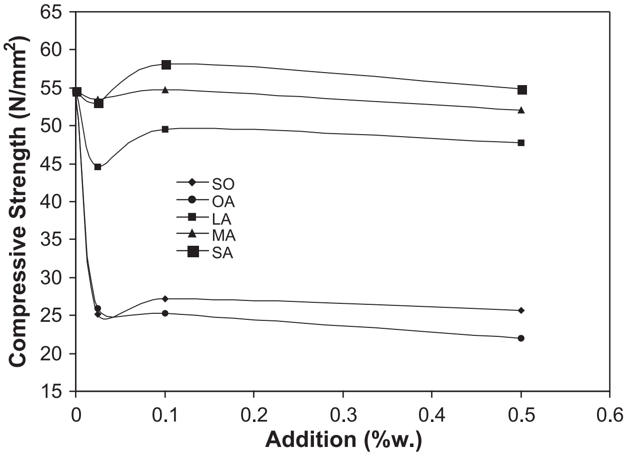


Fig. 2. The compressive strength values of the concrete containing the grinding aids at the age of 28 days.

In addition, as it can be seen from Figs. 2, 3 and 4, oleic acid decreased the compressive strength of the normal concrete more than sunflower oil. As the amount of the unsaturated fatty acids decreased, the compressive strength of the cement increased. Lauric acid decreased the strength of the cement in less degree than sunflower and oleic acid. Figs. 2, 3 and 4 also show that myristic acid and stearic acid both increased the compressive strength of the cement.

Myristic acid and stearic acid increased the compressive strength. Between these two saturated components, SA raises the compressive strength definitely and that value was 58.1 N/mm$^2$ at 0.1 wt.%. From these experimental results, it can be stated that as the carbon number in the chain of the saturated fatty acid molecule increases, the positive effect of that on the strength of the cement increases. The compressive strength of the concrete with MA and SA decreased in the range of 0.1–0.5 wt.%. In Fig. 3, there is a similar trend to Fig. 2. The 2-day strength values for the concrete with MA and SA are generally higher than that of the normal concrete, except for the others. In Fig. 4, the 7-day strength values are low except that the compressive strength value of the concrete made of the cement substituted with 0.1% SA is above that of the normal concrete.

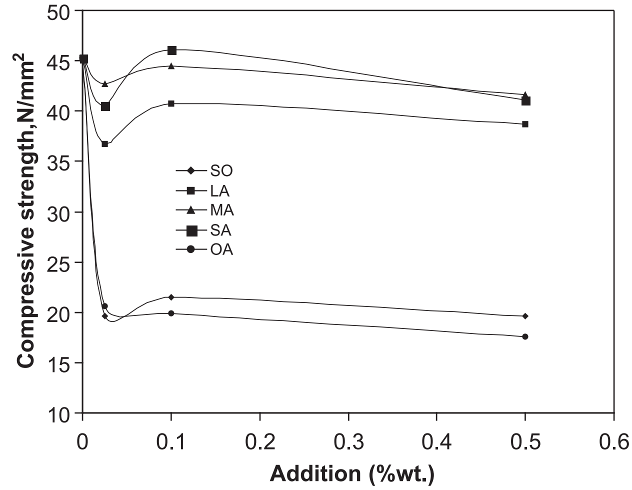


Fig. 4. The compressive strength values of the concrete samples at the age of 7 days.

Fig. 5, which relates the surface area to the addition, indicates that for the additives of LA, SA and OA, the specific surface of the cement increased up to 0.025 wt.%, for the others, the specific surface of the cement increased up to 0.1 wt.% and then decreased. The increase in the Blaine surface of the cement ground with SA is by 8.67% at 0.025 wt.%. With respect to the data, the addition of 0.5 wt.% for usage is practically unnecessary.

## 4. Conclusions

(1) The unsaturated fatty oils and their unsaturated fatty acid fractions, such as oleic acid, linoleic and linolenic acids, decrease excessively the compressive strength of the normal concrete. Sunflower oil and its unsaturated fatty acid fractions cannot be used as grinding aids in cement industry.

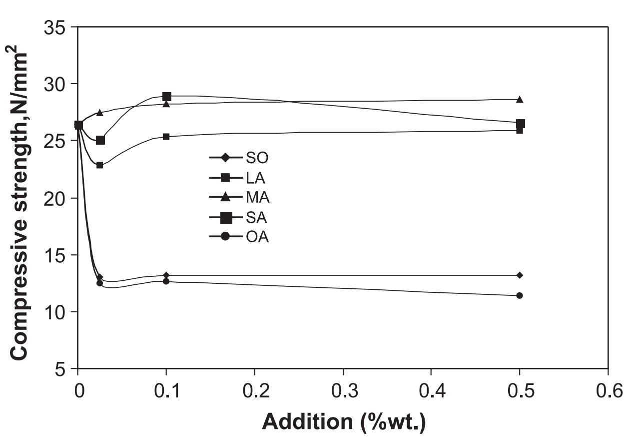


Fig. 3. The compressive strength of the concrete samples at the age of 2 days.

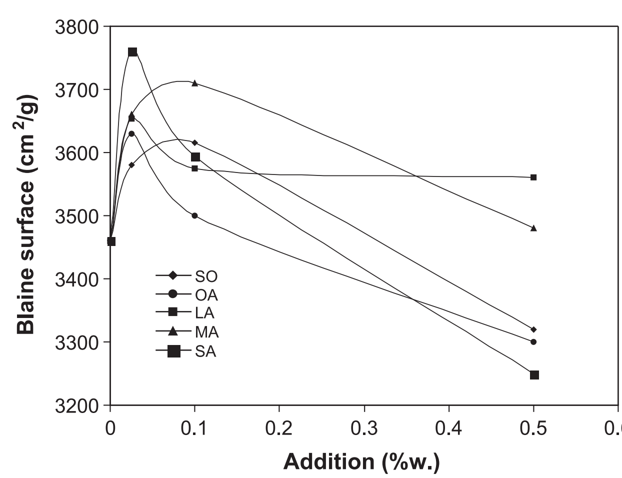


Fig. 5. The specific surface of the cement with the grinding aids.

(2) The saturated oil acids increase the compressive strength of the normal concrete in the order: stearic acid>myristic acid>lauric acid. That is, it increased with an increase in the chain length of the saturated oil acids. Nevertheless, lauric acid cannot be used because it decreases the compressive strength compared to the normal concrete.

(3) For an optimum addition, the grinding aids affect on the surface area of the normal cement in the order: stearic acid>myristic acid>lauric acid>oleic acid >sunflower oil. Myristic acid and stearic acid can be used as grinding aid.

(4) To use over 0.1 wt.% of the saturated fatty acid addition as grinding agent to the cement decreases the strength.

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